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13. ABSTRACT (Maximum 200 Words) Site characterization represents the initial phase of the active monitoring process that occurs as part of intrinsic organic contaminant bioremediation efforts. Initial characterization work sets the stage for evaluating the progress of the natural transformation of contaminants. The following have frequently been observed: parent compound disappearance, active microbial populations with biotransformation capabilities, and the appearance or disappearance of organic and inorganic constituents that provide evidence of bioremediation at contaminated sites. Quantitative evidence is lacking, however, for net removal of toxic compounds from complex mixtures solely by biological processes. This is due largely to the reliance on monitoring well samples for evidence of biological activity, rather than on identifying the mass of contaminants (and total reactive organic carbon) and estimating the net removal/transformation of reactive compounds over time. A dynamic approach to quantitative site characterization is needed that recognizes intrinsic bioremediation as an active cleanup approach. Careful attention must be paid to the identification of the three-dimensional distribution of contaminant mass. Then the correspondence between contaminant distribution and favorable physical, geochemical, and microbial conditions in the subsurface over time provides a basis for net contaminant-removal estimates. Mere adaptations of detective ground-water monitoring networks are insufficient for quantitative evaluation of intrinsic bioremediation technologies.				
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Site Characterization: What Should We Measure, Where (When?), and Why?

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Abstract

Site characterization represents the initial phase of the active monitoring process that occurs as part of intrinsic organic contaminant bioremediation efforts. Initial characterization work sets the stage for evaluating the progress of the natural transformation of contaminants. The following have frequently been observed: parent compound disappearance, active microbial populations with biotransformation capabilities, and the appearance or disappearance of organic and inorganic constituents that provide evidence of bioremediation at contaminated sites. Quantitative evidence is lacking, however, for net removal of toxic compounds from complex mixtures solely by biological processes. This is due largely to the reliance on monitoring well samples for evidence of biological activity, rather than on identifying the mass of contaminants (and total reactive organic carbon) and estimating the net removal/transformation of reactive compounds over time.

A dynamic approach to quantitative site characterization is needed that recognizes intrinsic bioremediation as an active cleanup approach. Careful attention must be paid to the identification of the three-dimensional distribution of contaminant mass. Then the correspondence between contaminant distribution and favorable physical, geochemical, and microbial conditions in the subsurface over time provides a basis for net contaminant-removal estimates. Mere adaptations of detective ground-water monitoring networks are insufficient for quantitative evaluation of intrinsic bioremediation technologies.

Introduction

The practice of site characterization for remediation of subsurface organic contaminants has evolved slowly in the past decade. Early guidelines (1-3) for minimal ground-water contamination detection monitoring (i.e., monitoring wells upgradient and downgradient) have been applied to many sites of potential concern from detection through remedial action selection phases.

This minimal approach has been applied widely, regardless of the physicochemical characteristics of contaminant mixtures or the complexity of hydrogeologic settings. With soluble inorganic constituents, this approach may be adequate for detection purposes, but assessment efforts require substantially more comprehensive approaches. For organic contaminant assessment efforts (i.e., determinations of the nature and extent of contamination), wells alone have been found to be inadequate monitoring tools. Recognition of the value of subsurface soil vapor surveys for volatile organic components of fuel and solvent mixtures has generated a flurry of modified site characterization approaches based on monitoring wells (4). These approaches to site characterization and monitoring network design suffer also from a failure to identify the total mass of contaminant in the subsurface.

This failure occurs for three main reasons. First, although volatile organic compounds (VOCs) are mobile in ground water and are frequently early indicators of plume movement (5), their detection in vapor or well samples and their apparent aqueous concentration distribution do not identify the total mass distribution of organic contaminant (6). Second, efforts to correlate observed soil vapor or ground-water VOC concentrations with those in subsurface solid cores have often been unsuccessful, because current bulk jar collection/refrigeration at 4°C guidelines for solid core samples for VOC analyses lead to gross negative errors (7). Third, "snapshots" (i.e., one-time surveys) of background and disturbed ground-water chemistry conditions have been interpreted as "constant," ignoring temporal variability in subsurface geochemistry.

The unhappy result of the slow improvement in site characterization and monitoring practices has often been the very low probability of detecting the source of mobile organic contaminants. This outcome may be followed by the misapplication of risk assessment or remediation models and fiscal resources. Nonetheless, good reasons exist for a more optimistic view of the future reliability of site-characterization and monitoring efforts.

The shortcomings of previous contaminant detection and assessment efforts have been recognized. New guidelines and recommendations for network design and operations will lead to more comprehensive, cost-effective site characterization (7, 8) in general. Also, excellent reviews of characterization and long-term monitoring needs and approaches in support of *in situ* remediation efforts should guide us in this regard (9, 10). Site characterization efforts provide a basis for long-term monitoring design and actually continue throughout the life of a remediation project.

Advanced Site Characterization and Monitoring

How do we estimate the potential for subsurface intrinsic bioremediation success and track its performance into the future? Clearly, we should seek to design technically defensible characterization and monitoring networks that will provide reasonable estimates of in-place contaminant distributions over time. Therefore, a dynamic, ongoing site-characterization effort includes the following objectives:

- Identify the spatial distribution of contaminants, particularly their relative fractionation in subsurface solids, water, and vapor, along potential exposure pathways, recognizing that the mass of contaminants frequently resides in the solids.
- Determine the corresponding spatial distribution of total reactive organic matter (e.g., degradable normal, aliphatic, and aromatic hydrocarbon compounds), because overall microbial activity and disruptions in subsurface geochemical conditions (and bioremediation indicators) are due to the total mass of reactive organic carbon.
- Estimate the temporal stability of hydrogeologic and geochemical conditions that may favor microbial transformations in background, source, and downgradient zones during the first year of characterization and monitoring.

- Derive initial estimates of net microbial transformations of contaminant-related organic matter over time that may be built into an efficient long-term monitoring network design.

The first three objectives establish the environment of major contamination and the conditions under which bioremediation may occur. The latter two objectives are vitally important, because evaluating the progress of intrinsic bioremediation processes depends on distinguishing compound "losses" due to dilution, sorption, and chemical reactions from microbial transformations. This approach has been suggested emphatically by Wilson (9) and was recently developed into a draft technical U.S. Air Force (USAF) protocol by Wiedemeier et al. (10).

The latter reference focuses directly on the implementation of intrinsic remediation for dissolved fuel contamination in ground water. The general approach is shown in Figure 1, which has been modified from the original work. The draft USAF protocol (10) has as its goals the collection of data necessary to support:

- Documented loss of contaminants at the field scale
- The use of chemical analytical data in mass balance calculations
- Laboratory microcosm studies using aquifer samples collected from the site

These data, if collected in three dimensions for an extended period, should be sufficient to implement intrinsic remediation successfully (11). The data collected in the initial site characterization effort (Figure 1) support the development of a site-specific conceptual model. This model is a three-dimensional representation of the ground-water flow and transport fields based on geologic, hydrologic, climatologic, and geochemical data for a site. The conceptual model, in turn, can be tested, refined, and used to determine the suitability of intrinsic remediation as a risk-management strategy. The validity of the conceptual model as a decision tool depends on the complexity of the actual hydrogeologic setting and contaminant distributions relative to the completeness of the characterization database. The draft USAF protocol is quite comprehensive in identifying important parameters, inputs, and procedures for data collection and analysis. The major categories of necessary data are listed in Table 1 from the draft protocol (10). Ongoing work on the protocol has revised some of the detailed guidance it provides on sampling and analytical protocols for these critical parameters; thus, recent drafts of the protocol should be even more useful to practitioners.

Typical detective monitoring data sets available prior to in-depth site characterization are more likely to contain contaminant-related information rather than the three-dimensional aquifer property, hydrogeologic, or geochemical data needed to formulate a conceptual model. A recognition of the variability inherent in these parameter distributions is critical to site characterization efforts.

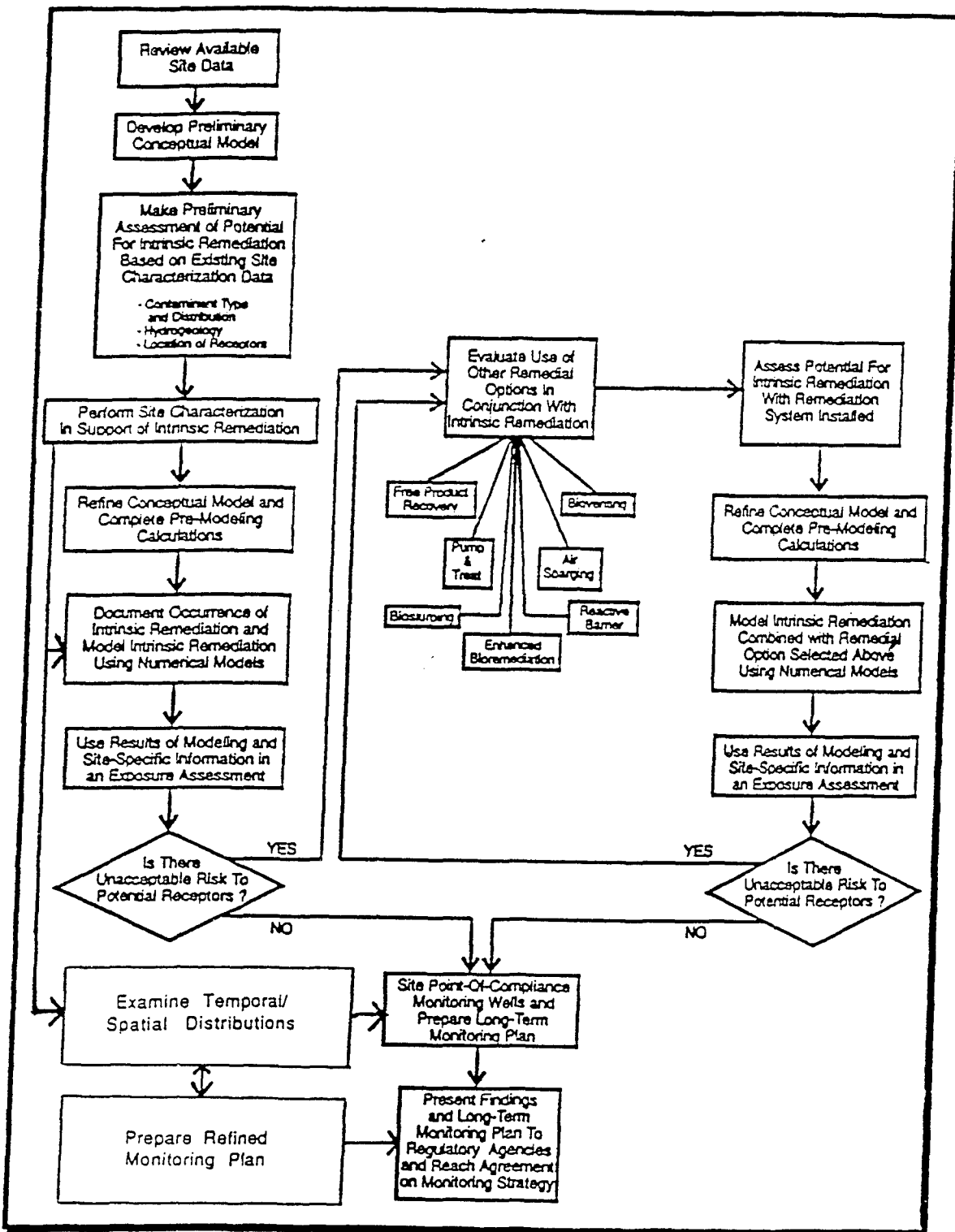


Figure 1. Intrinsic remediation flow chart.

Table 1. Site-Specific Parameters To Be Determined During Site Characterization (10)

<p>Fractionation and Spatial Extent of Contamination</p>	<p>Extent and type of soil and ground-water contamination</p> <p>Location and extent of contaminant source area(s) (i.e., areas containing free- or residual-phase product)</p> <p>Potential for a continuing source due to leaking tanks or pipelines</p>
<p>Hydrogeologic and Geochemical Framework</p>	<p>Ground-water geochemical parameter distributions (Table 2)</p> <p>Regional hydrogeology, including:</p> <ul style="list-style-type: none"> - Drinking water aquifers - Regional confining units <p>Local and site-specific hydrogeology, including:</p> <ul style="list-style-type: none"> - Local drinking water aquifers - Location of industrial, agricultural, and domestic water wells - Patterns of aquifer use - Lithology - Site stratigraphy, including identification of transmissive and nontransmissive units - Grain-size distribution (sand versus silt versus clay) - Aquifer hydraulic conductivity determination and estimates from grain-size distributions - Ground-water hydraulic information - Preferential flow paths - Location and type of surface water bodies - Areas of local ground-water recharge and discharge <p>Definition of potential exposure pathways and receptors</p>

Sampling in Space

The initial site characterization phase should be designed to provide spatially dense coverage of critical data over volumes corresponding to 10-yr to 100-yr travel times along ground-water flow paths. If the flow path intersects a discharge zone in less than 100 yr, then the volume should be scaled accordingly. For example, if the flow path discharges after 10 yr, the critical volume would be 1 yr of travel time. The "volume-averaged" values of the contaminants, hydrogeologic and geochemical parameters within zones along the flow path(s), should be derived from data sets that are large enough to permit estimation of statistical properties (e.g., mean, median, correlation distance, and variance). In general, this means that the data sets for

derived mass loadings of contaminants, aquifer properties, and geochemical constituents (Table 2) derived from spatial averages of data points must include approximately 30 or more data points (12-14). Indeed, this minimum data-set size strictly applies to points in a plane.

Table 2. Target Constituents for Site Characterization in Support of Intrinsic Bioremediation

Contamination Area	Apparent/Geochemical Redox Zone	Contaminant Mixture	Inorganic Constituents	Intrinsic Constituents
Source	Reducing	Fuels Chlorinated solvents	O ₂ , CO ₂ , H ₂ S; pH, Fe ²⁺ , HS ⁻ /S ⁼ , NO ₂ ⁻ , NH ₃ , alkalinity	Organic carbons, CH ₄ , organic acids, phenols As above and: chlorinated metabolites, ethylene, ethane
Downgradient	Transitional/ Suboxic	Fuels Chlorinated solvents	O ₂ , CO ₂ , H ₂ S; pH, Fe ²⁺ , alkalinity, NO ₂ ⁻ , NO ₃ ⁻ , NH ₃ , HS ⁻ /S ⁼	Organic carbon, CH ₄ , organic acids, phenols As above and: chlorinated metabolites, ethylene, ethane
Upgradient/ Far-field downgradient	Oxic	Fuels Chlorinated solvents	O ₂ , CO ₂ , H ₂ S; alkalinity, Fe ²⁺ , NO ₃ ⁻ , NO ₂ ⁻ , NH ₃	Organic carbon, CH ₄ , organic acids, phenols As above and: chlorinated metabolites, ethylene, ethane

Two major decisions must be made with regard to how spatially averaged masses of contaminants, electron donors (e.g., organic carbon, Fe²⁺, S⁼, and NH₃), and electron acceptors (e.g., O₂, NO₃⁻, NO₂⁻, Fe and Mn oxides, and SO₄⁼) are to be estimated.

The first question deals with identification of the media in which the bulk of the constituent's mass resides. For aquifer properties (e.g., grain size and laboratory estimates of hydraulic conductivity), the answer is simple. In this case, the solids are clearly the media of interest. For constituents, particularly VOCs, which are sparingly water soluble, the bulk of the mass may in fact reside in the solids, though both solids and water samples must be collected carefully.

The second question pertains to the depth interval over which "planar" data points might be averaged. With fuel-related aromatic contaminants, the depth interval above and below the capillary fringe/water table interface typically exhibits order-of-magnitude differences in solid-associated concentrations. In this situation, averaging data points over depths greater than 0.5 m could easily lead to order-of-magnitude errors in estimated masses for a site. Continuous coring of subsurface solids and close interval (i.e., <1 m) sampling of water should be considered in many VOC investigations. To approach this level of depth detail in sampling, "push" technologies and/or multilevel sampling devices present very useful tools for site characterization. Push technologies rely on hydraulic or hammer-driven, narrow diameter (i.e., <2 in.) probes for solid or water sampling. These technologies have the potential to provide greater spatial coverage of the subsurface at less cost than drilling techniques.

The approach to site characterization for chlorinated hydrocarbons is significantly more difficult. Very few models of site characterization for these contaminants have estimated mass loadings in specific media. Many of the previously referenced methods may work satisfactorily. Free-phase detection, assessment, and quantitation, however, may be more a matter of luck and exhaustive sampling than intuition based on experience.

Sampling Over Time

VOC compounds (e.g., aromatic hydrocarbons and chlorinated solvents) are among the target contaminants that are considered constituents of concern in remedial investigations. Their aqueous solubility and demonstrated association with aquifer solids require sampling of these media during the site characterization phase. This suggestion also applies to organic metabolites of complex organic mixtures (e.g., ethylene, vinyl chloride, aromatic acids, and phenols). Aqueous plumes that develop subsequent to the release of these organic mixtures and byproduct compounds have received the most attention in the past. The fact that the mass of these contaminants frequently resides in the solids strongly suggests that the solids should receive the most attention in the initial site characterization effort. This should also be the case for the physical, geochemical, and microbial determinations.

Initially, conventional nested monitoring wells with screened lengths of 1 m or more will be useful for estimating the spatial extent of the dissolved plume, for delineating apparent geochemical zones, and for providing data on water level and aquifer property (e.g., slug- and pump-test derived hydraulic conductivity estimates). Semiannual or annual sampling of wells, particularly multilevels appropriately designed and completed, should be quite useful over the course of the long-term monitoring program. Sampling should track the downgradient progress of risk-associated target compounds and permit testing predictions of intrinsic bioremediation effects on risk reduction.

Proof of the effects of the net removal of specific solid-associated contaminants due to intrinsic bioremediation, however, will depend on solid sampling and analysis at annual or greater intervals, because solid-associated concentrations may be expected to change slowly. Unless biotransformation can be shown to be a major loss mechanism for contaminants mainly in solids over extended periods, it will remain an area of research rather than practice.

Because very few contamination situations have been monitored intensively for periods exceeding several years, it is difficult to define specific sampling frequencies for the range of hydrogeologic

and contaminant combinations that may be encountered. The adoption and future refinement of recently developed, technically defensible protocols will improve intrinsic remediation approaches to risk management in subsurface contamination situations.

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